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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Substitution of Degraded Cellulose Derivatives for High Calorie Ingredients in Foods

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ABSTRACT OF THE DISCLOSURE:

A method of reducing the caloric content of a food stuff composition is disclosed, which comprises the substitution of a mixture of oligomers derived from degradation of a cellulose derivative for at least a portion of the fat, sugar, carbohydrate or other highly caloric ingredient contained in the foodstuff. The mixture of oligomers which is used as a substitute has an average degree of polymerization in the range of 3 to 300 and an average molecular weight in the range of 500 to 100,000. Also disclosed are low calorie food products obtained by this method, which products are acceptable to the consumer.

FIELD OF THE INVENTION

The present invention generally relates to the substitution of degradation products of cellulose derivatives for a substantial portion of the normal fat, sugar, carbohydrate or other highly caloric substance contained in a food product, in order to reduce the caloric content of this food product.

The invention more particularly relates to a method of preparing low calorie food products by substituting a new degradation products of cellulose derivations for a substantial portion of the fat, sugar, carbohydrate contained in these products, and to the low calorie food products that are so prepared.

BACKGROUND OF THE INVENTION

Cellulose derivatives such as carboxymethycellulose, methylcellulose, methylethylcellulose, hydroxypropylmethylcellulose and hydroxypropylcellulose are non-caloric (non-metabolizable by humans or intestinal flora in human beings), odorless, tasteless water-soluble polymers derived from cellulose. These cellulose derivatives may act as thickeners, binders, stabilizers, suspending agents or flow control agents. They form films resistant to oils, greases and organic solvents.

They dissolve rapidly in cold and hot water and are physiologically inert. In theory, the non-caloric nature of cellulose derivatives would suggest that they might be used as filler materials or substitutes for fat, sugar, carbohydrate or other high calorie components of normal food products. However, the simple substitution of such non-toxic non-caloric substances for a high calorie food component, is not practicable because any substantial substitution of a normal food ingredient will typically alter one or more of the color, volume, texture, structure, mouthfeel, odor or flavor of the food to such an extent as to render the food product unacceptable to a consumer.

Degradation of cellulose derivatives is normally considered undesirable and to be avoided. Cellulolytic and viscosity reducing treatments on cellulose derivatives have been deliberately avoided in the past and high molecular weight products deliberately produced. Indeed, non-degraded cellulose derivatives have been incorporated into food stuff compositions as disclosed in U.S. Patent No. 4,214,009 to Chang.

Enzymatic hydrolysis of cellulose derivatives have been studied in the past in the context of synergism studies among combinations of enzymes, the possible indexing of substituent distribution patterns, the effect of various substituents on enzymatic hydrolysis and the like. Such studies have been published in the following: Chouchon et al., Biotech. Bioeng.,

Vol. 26, pp. 988-991 (1984); Henrissat et al., Biotechnology, Vol. 3, pp. 722-726 (1985); Chetkarov et al., Monatshefte Fur Chemie, Vol. 116, pp. 1433-45 (1985); Chetkarov et al., Monatshefte Fur Chemie, Vol. 117, pp. 1021-1026 (1986); Wirick, J. Polym. Sci., Part A-1, Vol. 6, pp. 1195-1974 (1968); Bhattacharjee, J. Polym. Sci., Part C, Vol. 36, pp. 509-521 (1971). Reduction of chain length determinations have also been studied. Almin et al., Arch. Biochem. Biophys., pp. 124, 129 (1968); Ghose, Biotech. Bioeng., Vol. 11, pp. 239 (1969).

In copending Canadian patent application nos. and filed on the same day as the instant application, there are disclosed and claimed novel water soluble or water suspendable mixtures of relatively low molecular weight polymers or oligomers derived from cellulose derivatives as well as fractions of the mixtures of oligomers obtained from the initial degradative process.

The oligomeric mixtures can be made from several different cellulose derivatives, the most preferred raw material being carboxymethylcellulose. The oligomeric mixtures can be prepared by different modified and unmodified cellulolytic enzymes, the most preferred sources of the enzyme being strains of Trichoderma reesei, Aspergillus and Penicillium.

More particularly, the above mentioned copending applications disclose and claim a water soluble mixture of oligomers derived from a cellulose derivative comprising a cellulose derivative degraded to form a mixture of oligomers having an average degree of polymerization in the range of 3 to 300 and an average molecular weight of 500 to 100,000. The soluble cellulose derivative is preferably selected from the group of carboxymethylcellulose, methylcellulose, methylethylcellulose, hydroxypropylmethylcellulose and hydroxypropylcellulose and mixtures thereof.

The cellulose derivative may be degraded by enzymatic, chemical or physical agents/mechanisms. In embodiments where an enzyme preparation is utilized, the enzyme preparation is typically selected from the group of cellulases, modified cellulases and mixtures thereof.

In embodiments where degradation of a cellulose derivative is to be effected by chemical or physical means, chemical hydrolysis, chemical oxidation and physical depolymerization are preferred mechanisms for achieving the desired oligomeric mixtures according to the invention.

An enzyme preparation may be a cellulase or modified cellulase (i.e., modified to remove or prevent the formation of mono- and disaccharides producing enzymes in the cellulase preparation in the first instance, e.g., by genetic alteration of the microorganism from which the cellulase preparation is prepared) preferably produced from microorganisms selected from the group of Trichoderma, Aspergillus and Penicillium. Most preferably a cellulase preparation is derived from Trichoderma reesei from which at least one of beta-glucosidase and cellobiohydrolase activities have been removed. An enzyme preparation most preferably comprises endo-1,4-beta-glucanase.

In the above mentioned copending patent applications, there is also disclosed a method for producing a mixture of oligomers from cellulose derivatives comprising the steps of: selecting a cellulose derivative; selecting a cellulolytic agent which degrades the selected cellulose derivative into a mixture of oligomers having an average degree of polymerization in the range of 3 to 300 and a molecular weight in the range of 500 to 100,000; and reacting the selected cellulolytic material with the selected cellulose derivative for a time and at a temperature sufficient to produce the mixture of oligomers. The cellulose derivative is preferably selected from the

group of carboxymethylcellulose, methylcellulose, methylethylcellulose, hydroxypropylmethylcellulose, hydroxypropylcellulose and mixtures thereof.

The step of selecting the cellulolytic agent may comprise selecting a hydrolytic chemical or mixture of chemicals such as a hydrolytic acid or base treatment solution (e.g. containing H_2SO_4, HCl, NaOH or NH_4OH) or an oxidative chemical or chemical solution (e.g. solutions containing oxygen, hydrogen peroxide, ozone or mixtures thereof).

The step of selecting the cellulolytic agent may also comprise selecting a microorganism which produces a cellulolytic material and preparing a cellulolytic material from a culture of the microorganism. The cellulolytic material produced by the microorganism may be purified to remove enzymes which will react with the cellulose derivative to produce mono- and disaccharides. The microorganism is preferably selected from the group of Trichoderma, Aspergillus and Penicillium. In order to prevent hydrolysis of the cellulose derivative into mono- and disaccharides the selected microorganism may alternatively be treated to alter the genes of the microorganism such that production of mono- and disaccharide generating enzymes by the genes is disenabled.

SUMMARY OF THE INVENTION

The present invention is based on the discovery that the novel oligomeric mixtures and fractions thereof of the above mentioned copending patent applications are especially useful as fat, carbohydrate, high calorie ingredient, calorie saving or low caloric substitutes in a wide range of foodstuffs.

More particularly, the present invention proposes

to use novel low molecular weight polymers or oligomeric mixtures obtained by degradation of cellulose derivatives, to replace a substantial portion of high caloric ingredients in conventional foodstuff or recipes and thus obtain an end food product which is acceptable to the consumer in terms of eating quality, i.e. flavor, odor, mouthfeel, texture, etc. The relatively low molecular weight polymer, oligomeric mixtures and fractions (of the total mixture of oligomers into further separated mixtures of oligomers of varying chain length) used in the present invention are more advantageous for applications in food than the high molecular weight cellulose derivative.

The invention thus proposes a method for preparing a low calorie foodstuff, comprising:

<u>either</u> removing all or a portion (typically up to 50% by weight) of a selected fat contained in a foodstuff and substituting a mixture of oligomers produced as disclosed hereinabove for the removed fat;

<u>and/or</u> removing up to about 40% of a selected carbohydrate contained in a foodstuff and substituting a mixture of oligomers produced as disclosed hereinabove for the removed carbohydrate.

The invention also contemplates <u>either</u> separating a mixture of oligomers initially produced by a cellulolytic agent or process according to the invention into fractions of oligomers of different average molecular weight, removing all or at least a portion (typically up to 50% by weight) of a selected fat contained in a foodstuff, and substituting one or more of the fractions for the removed fat; <u>and/or</u> separating a mixture of oligomers initially produced by a cellulolytic agent or process according to the invention into fractions of oligomers of different average molecular weight, removing up to 40% by weight of a selected carbohydrate contained in a foodstuff and substituting one

or more of the fractions for the removed carbohydrate.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows molecular weight distribution patterns of a methylcellulose and its hydrolysate as described in Example 2a herein;

FIG. 2 shows molecular weight distribution patterns of hydroxypropylmethylcellulose and its hydrolysate as described in Example 2b herein;

FIG. 3 shows molecular weight distribution patterns of a carboxymethylcellulose and its hydrolysate as described in Example 2c(i) herein;

FIG. 4 shows molecular weight distribution patterns of a carboxymethylcellulose and its hydrolysate as described in Example 3 herein;

FIG. 5 shows molecular weight distribution patterns of selected fractions of the carboxymethylcellulose hydrolysate as described in Example 3 herein.

DETAILED DESCRIPTION OF THE INVENTION

The substitute used in the method according to the invention is a water soluble or suspendable mixture of oligomers derived from a cellulose derivative and its fractions. The oligomeric mixtures are characterized by having an average degree of polymerization (DP) in the range of 3-300 and a molecular weight in the range of 500-100,000.

Following is a description of some exemplary embodiments of the invention where a cellulolytic treatment is carried out using enzymatic, chemical or physical agents/methods. Insofar as enzymatic treatments are concerned, the following description also includes a most

preferred protocol for initial preparation of an enzyme.

In one embodiment, a selected cellulose derivative may be hydrolyzed by treating the cellulose derivative with a solution of acid or base. Typical acid treatment solutions might contain sulphuric acid, hydrochloric acid, phosphoric acid, nitric acid or mixtures of two or more of the foregoing. Typical base solutions might contain a hydroxide ion containing or producing material such as an alkali hydroxide (e.g. sodium hydroxide), ammonium hydroxide, and mixtures of two or more of the foregoing. The concentration of the acid or base in the treatment solution and the treatment time and temperature may vary depending on the degree of degradation of the cellulose derivative which is desired. The person skilled in the art will recognize that higher acid or base concentrations, treatment times and treatment temperatures will generally result in a higher degree of degradation of the cellulose derivative (i.e. an oligomeric product mixture having a lower average DP and molecular weight). And, lower acid or base concentrations and treatment times and temperatures will generally produce oligomeric product mixtures of higher average DP and molecular weight. In any even where an acid or base hydrolysis treatment is utilized, the acid or base concentration and the treatment time and temperature is selected to produce a mixture of oligomers having an average DP of between 3 and 300, an average molecular weight of between 500 and 100,000 and which most preferably contains less than about 25% by weight of mono- and disaccharides such as flucose and cellobiose.

In another embodiment a selected cellulose derivative may be degraded by oxidation with such agents as oxygen or hydrogen peroxide in basic solution or with ozone. Such oxidative treatments and reaction conditions are well known in the art. Gaseous agents such as oxygen or ozone

would typically be bubbled continuously through the solution for a suitable time and at a suitable temperature. An oxidative treatment with peroxide might comprise treating a selected cellulose derivative with a solution of hydrogen peroxide of suitable concentration and at a suitable temperature.

The oligomeric mixtures may also be produced by physical (mechanical) depolymerization methods such as by subjecting a solution of a selected cellulose derivative to treatment with relatively high frequency sound waves with a sonicator. Other physical treatments well known in the art such as chopping or shearing a selected cellulose derivative with, for example, a high speed mixer or homogenizer may be employed to effect depolymerization.

Whatever conventional chemical (hydrolytic, oxidative or otherwise) or physical treatments are employed, the conditions and the degree of treatment are selected such that the

oligomeric mixture resulting from the initial treatment has an average DP of between 3 and 300, an average molecular weight of between 500 and 100,000 and contains less than about 25% by weight of mono- and disaccharides and most preferably less than about 10% by weight of mono- and disaccharides.

Enzyme Preparation

Enzymes which may be used in some embodiments of this invention are various food-grade cellulase preparations. They can be produced from a multitude of different microorganisms such as strains of *Trichoderma*, *Aspergillus*, *Penicillium*, etc. A selected microorganism strain is grown by conventional means in a medium containing food grade materials such that the cellulases are produced, the microorganism is separated from the medium, the medium is collected and typically concentrated and dried. These enzymes can be used as such or in mixtures and they can be modified in many different ways known to the man skilled in the art. A most preferred enzyme preparation is produced from *Trichoderma reesei*, from which preparations the beta-glucosidase and/or the cellobiohydrolase activities are removed chromatographically or genetically. Beta-glucosidase and/or cellobiohydrolase activities are preferably removed from the selected cellulase preparation so as to prevent the degradation of the cellulose derivative into mono- and disaccharides. Genetic alteration of the appropriate enzyme

producing microorganism may be effected with radiation or mutagenic chemical agents (or by gene inactivation by recombinant DNA methods) so as to disenable production of beta-glucosidase and cellobiohydrolase by the microorganism. Cellulase preparations suitable for use herein are, e.g., the commercially available cellulase preparations designated as the Econase series as produced by Alko Ltd., Helsinki Finland.

Starting Materials

Preferred cellulose derivatives for use herein are carboxymethyl-, methyl-, methylethyl-, hydroxypropylmethyl- or hydroxypropylcellulose and any combinations thereof. The invention is not limited to the use of these cellulose derivatives.

General Preparation of a Typical Hydrolysate

In one embodiment, cellulose derivative hydrolysates may be prepared from soluble cellulose derivatives as defined above by an enzymatic hydrolysis utilizing a cellulase preparation having endo-1,4-beta-glucanase as the sole active hydrolytic agent such that only insignificant amounts of mono- and disaccharides which are absorbed in human intestine (e.g., glucose) or hydrolyzed by the intestinal bacterial flora (e.g., cellobiose), are produced. On the other hand the average degree of polymerization (DP) of the oligomers

formed by such a hydrolysis is lower than 300, and thus the viscosity of solutions of the hydrolysate is reduced significantly compared to the viscosity of solutions of the unhydrolysed cellulose derivatives. The specific conditions suitable for and the specific time sufficient to secure the desired hydrolysis may be readily determined for each selected cellulose derivative and each selected enzyme preparation.

Similarly in other embodiments where degradation is carried out using chemical or physical means, the average DP of the oligomers is less than 300 and the viscosity of the resulting mixture is significantly reduced. Most preferably in such embodiments, the treatment conditions are selected such that the resulting oligomeric mixtures contain less than about 5% by weight of mono- and disaccharides.

Use of Oligomeric Mixtures Derived from Cellulose Derivatives

The degraded cellulose derivative products obtained as disclosed hereinabove (and fractions thereof) dissolve rapidly in cold and hot water and are physiologically inert. Such initially formed oligomeric mixtures and selected fractions may act as thickeners, binders (e.g. in coating applications such as in the formation of conductive particle filled coatings on electrodes), stabilizers, suspending agents or flow control agents, or fillers in wide variety of applications such as in

cosmetics, pharmaceuticals, plastics, paper and the like. Such products may also form films resistant to oils, greases and organic solvents and may be useful as organic resistant coatings such as coatings on clothing, paper and the like.

The cellulose derivatives used as starting materials in the present invention are as such non-caloric. Because a degradative treatment according to the present invention does not produce significant amounts of metabolizable sugars, the resulting oligomeric mixtures according to this invention with their improved properties, are especially useful as low-caloric substitutes in food stuffs.

Thus, the oligomeric mixtures and fractions thereof produced as disclosed hereinabove can be used for example as new low-caloric fat sparing agents or bulking agents. These mixtures can be used to replace fat in various food stuffs, like baked goods, butter icing and custard. All of and at least a substantial portion of fat can be replaced by these mixtures. The amount which can be replaced depends on the application. The texture of the food stuff and the eating quality of the new product can thus be improved or remain unchanged.

Oligomeric mixtures and fractions thereof produced as disclosed hereinabove can be used also as new low-caloric bulking agents. These mixtures can be used to replace carbohydrates such as sugar in different kinds of baked

products or in other food stuffs. The amount of carbohydrate replaced with these mixtures depend on the application and average chain length of the oligomers.

By conventional means an initially degraded cellulose derivative mixture may be further separated into fractions of oligomers of differing average chain lengths. The viscosity of the various fractions will vary with the degree of average chain length of the oligomers contained within a fraction. Depending on the particular food stuff application, the invention further contemplates selecting one or more fractions from an initial oligomeric mixture having a viscosity (average chain length) which is most appropriate for the particular food stuff application. The selection of a particular average chain length fraction and the amount of such a fraction to be used in any given food stuff application may vary according to the amount of fat or carbohydrate to be replaced, it being recognized that the higher the absolute amount of substitution agent desired to be used in a particular foodstuff, the lower the viscosity (average molecular weight) of the fraction of mixture of oligomers should be used.

It is to be further recognized that an oligomeric mixture falling within a particular range of viscosities may be preferred in any particular food recipe insofar as it may be desirable to obtain an end product which resembles the eating quality of the normal recipe containing the normal relatively

high level of fat or other high calorie ingredients.

The following examples 1-4 set forth typical exemplary routines for preparing a cellulase and various cellulose derivative hydrolysates therefrom.

Example 1 -- Typical Cellulase Preparation

The beta-glucosidase activity was removed by ion exchange chromatography from the commercially available cellulose preparation, Econase CE, as so designated by Alko Ltd., Helsinki, Finland which was produced from a strain of Trichoderma reesei. The cellulase preparation (column A, Table 1) was passed through a cation exchange column (S-Sepharose FF, Pharmacia, LKB Biotechnology AB, Uppsala, Sweden) which was equilibriated with 50mM sodium acetate pH 3.8 equilibrium buffer. The unbound protein (including oligomer producing endoglucanases) was washed out with the equilibrium buffer (column B, Table 1). Beta-glucosidase activity remained bound to the column and could be separately eluted with 1M NaCl.

TABLE 1

Enzyme	Relative Enzyme Activity (%)	
	A	B
	before ion exchange procedure	after ion exchange procedure
Beta-glucosidase	100	0
endo-1, 4, -beta-glucanase	100	70

Endo- 1, 4- beta-glucanase and beta-glucosidase activities were measured as described by Bailey & Nevalainen (1981): Enzyme Microb. Technol. 3: 153-157. The relative enzyme activities reported in Table 1 of the Econase preparations before and after passage through an ion exchange column demonstrate the results of a typical means according to the invention of preparing an essentially beta-glucosidase free preparation for use in producing the oligomeric hydrolysates contemplated by the invention.

Although Table 1 reports relative enzyme activities, the absolute amount of enzyme used in any particular example is hereafter reported in terms of the amount of enzyme activity of the enzyme employed according to the universal activity unit of nano-katal (nkat) which stands for that amount of enzyme which produces one nanomole of reaction product in one second. (In the context of this application a hydrolysate reaction product such as an oligomer which is capable of reducing an agent such

as dinitrosalicylic acid which is reduced by the hydrolysate reaction product and subsequently measured.) The method of Bailey et al., Enzyme Microb. Technol., (1981) 3: 153-157 describes how such measurements of enzyme activity can be made using glucose as a standard.

Example 2 — Cellulose Derivative Enzymatic Hydrolyses

a. Methylcellulose hydrolysate

30g of methylcellulose (MC, Methocel MC, 64630, Fluka Chemie AG, CH-9470 Buchs, Switzerland) was mixed in 3l of water and the pH of the solution was adjusted to 5.5 with 15% phosphoric acid and the temperature was raised to 40°C. 0.3ml of the enzyme preparation having a total endo-1, 4 beta-glucanase activity of 1680 nkat from which the beta-glucosidase activity was removed chromatographically (as described in Example 1) was added to the solution. After hydrolysis for 24 hours the enzyme was inactivated by heating (90°C, 15 min.). The hydrolysate solution was subsequently cooled and freeze-dried.

The hydrolysate product contained less than 0.5% by weight of glucose and cellobiose.

The molecular weight distribution patterns of methylcellulose, curve 10, and its hydrolysate, curve 20, are shown in FIG. 1.

The molecular weight distributions of the cellulose derivatives and their hydrolysates were determined by HPLC using a gel filtration column (TSK gel G2500PW, Toyo Soda Manufacturing Co., Ltd., Japan) with a refractive index detector (HP 1037 A) and Pharmacosmos Dextran Standards (Pharmacosmos, DK-4130, Viby Sj., Denmark). The eluent was 0.5M sodium chloride.

b. Hydroxypropylmethylcellulose Hydrolysate

20g of hydroxypropylmethylcellulose (HPMC, H-9262, Sigma Chemical Company, St. Louis, MO, U.S.A.) was mixed in 1l of water and the pH of the solution was adjusted to 5.5 with 15% phosphoric acid and the temperature was raised to 40°C. 0.24ml of the enzyme preparation having a total endo-1, 4 beta-glucanase activity of 1340 nkat from which the beta-glucosidase activity was removed chromatographically (as described in Example 1) was added to the solution. After two hours another 20g of hydroxypropylmethylcellulose was added to the solution. After the hydrolysis of 22 hours the enzyme was inactivated by heating (90°C, 15 min.). Finally the hydrolysate solution was cooled and freeze-dried.

The product contained less than 0.05% by weight of glucose and cellobiose.

The molecular weight distribution patterns of the hydroxypropylmethylcellulose, curve 30, and its hydrolysate,

curve 40, are shown in FIG. 2. The molecular weight distribution pattern was determined as described in Example 2A.

c. Carboxymethylcellulose Hydrolysate

(i) Hydrolysis with *Trichoderma reesei* derived enzyme preparation

20kg of carboxymethylcellulose (CMC 7MFD-type, a cellulose gum, also designated by the tradename Blanose and available from Hercules Chemical Company, 92507, Rueil-Malmaison Cedar, France; 7MFD designating a medium viscosity, food grade sodium carboxymethylcellulose having 7 out of 10 glucose units substituted with carboxymethyl) was mixed in 320l of water and the pH of the solution was adjusted to 5.5 with 15% phosphoric acid and the temperature was raised to 40°C. 0.27l of the enzyme preparation having a total endo-1, 4 beta-glucanase activity of 1,780,000 nkat from which the beta-glucosidase activity was removed chromatographically (as described in Example 1) was added to the CMC solution. After one hour another 20kg of CMC was added to the solution. After hydrolysis of 23 hours the enzyme was inactivated by heating (90°C, 15 min.). Finally, the hydrolysis solution was concentrated by conventional evaporating and spray-drying.

The product contained less than 2% by weight of glucose and cellobiose. When the same hydrolysis was carried out with the

original cellulase enzyme preparation of Trichoderma reesei-fungus, the amount of produced glucose and cellobiose was above 5% by weight.

The molecular weight distribution patterns of carboxymethylcellulose, curve 50, and its hydrolysate, curve 60, are shown in FIG. 3.

The molecular weight distribution pattern was determined as described in Example 2a.

(ii) Hydrolysis with Aspergillus and Penicillium derived enzyme preparations

The enzyme preparations selected were commercially available Cellulase AP 3 (Amano Pharmaceutical Co., Ltd., Nagoya, Japan) produced using an Aspergillus strain and Cellulase CP (Sturge Enzymes, North Yorkshire, England) produced using a Penicillium strain. Carboxymethylcellulose hydrolysates were prepared as described in Example 2c(i), except that 30g of CMC-7MFD was used in 1l of water, and the amounts of enzymes added were 0.028g of Cellulase AP 3 (having a total endo-1, 4 beta-glucanase activity of 1350 nkat) and 0.048g of Cellulase CP (having a total endo-1, 4 beta-glucanase activity of 1350 nkat). The viscosities and molecular weight distributions of the hydrolysates produced by either cellulase were similar (FIG. 3) to the hydrolysate produced with enzymes derived from Trichoderma reesei.

The viscosities of the various cellulose derivatives and their hydrolysates as described and prepared in Example 2 were measured using a Haake-Rotovisco viscometer with sensor systems NV (Karlsruhe, Federal Republic of Germany) (Table 2). The viscosities were measured in water solutions at 25°C. Table 2 sets forth the concentrations (by weight) of a variety of solutions all having the same viscosity.

TABLE 2

Concentrations of cellulose derivatives and their respective hydrolysates in solution all having a viscosity of 20mPa.s (milli-Pascals-second) at 25°C.

Cellulose Derivative	Concentration (by weight)
Methylcellulose	2%
Methylcellulose hydrolysate	5%
Hydroxypropylmethylcellulose	3%
Hydroxypropylmethylcellulose hydrolysate	10%
Carboxymethylcellulose	2%
Carboxymethylcellulose hydrolysate	20%

As the data in Table 2 indicates, the hydrolysate of a cellulose derivative has a substantially lower viscosity than an equal amount by weight in aqueous solution of the cellulose derivative itself. Thus, the hydrolysate can be incorporated

into a foodstuff in substantially higher quantity as a fat or sugar substitute than the cellulose derivative itself without compromising the texture, volume, density or the like of the foodstuff.

Example 3 — The Fractionation of Carboxymethylcellulose Hydrolysate

The carboxymethylcellulose hydrolysate was prepared as described in Example 2c(i), except that the raw material was CMC 7LFD (designating a low viscosity, food grade cellulose gum having 7 out of 10 glucose units substituted with carboxymethyl, designated under the tradename Blanose and available from Hercules Chemical Co., France) 1.6kg CMC was used in 8l of water and that the amount of enzyme added was 13.2ml having a total endo-1, 4 beta-glucanase activity of 87,000 nkat. 5ml of the hydrolysate (0.5g of dry matter) was further fractionated into three fractions by gel permeation chromatography (Pharmacia K 26/100 -column, Sephacryl S-200 -gel, Pharmacia LKB Biotechnology AB, S-75182 Uppsala, Sweden). The eluent was distilled water, the flow rate was 14 ml/hour, and the fractionation process was carried out for 45 hours and fractions collected at intervals of 0.5 hours and pooled into three fractions (18 hours - 26 hours, curve 90, 26 hours - 32 hours, curve 100, and 32 hours - 38 hours, curve 110, FIG. 5, respectively). The molecular weight distributions of carboxymethylcellulose, curve 70, carboxymethylcellulose

hydrolysate, curve 80, and the three further fractions, curves 90, 100, 110, FIGS. 4, 5, were determined by HPLC as described in Example 2.

Example 4 -- Chemical Hydrolysis

2 g of carboxymethylcellulose (Blanose Cellulose Gum 7 LFD, Hercules Chemical Co., 92507, Rueil-Malmaison Cedar, France) was hydrolysed for one hour in 100 ml of 1 M sulphuric acid solution at 100°C. After hydrolysis the solution was cooled to about room temperature, neutralized to about pH 6 with 25 ml (w/w) of NaOH solution and freeze-dried. This hydrolysis treatment produced a mixture of oligomers containing less than about 4% by weight of mono and disaccharides. The viscosity (and average DP) of this hydrolysate is similar to the viscosities (and average DP) of the hydrolysates produced by the enzymatic treatments described above utilizing enzymes derived from Trichoderma reesei.

Example 5 -- Specific Exemplary Formulations Wherein High Caloric Ingredient is Reduced

As described below a variety of polular high calorie food recipes were modified by substituting certain amounts of various carboxymethylcellulose hydrolysates for a certain portion of the normal level of a high calorie component of the food recipes. With respect to the invention, it is to be

understood that the replacement of a high caloric ingredient is not limited to any particular cake, spread, icing, mayonnaise or other food recipe as may be specifically set forth herein for purposes of example. The various carboxymethylcellulose hydrolysates employed as substitutes or additives in the food recipes described hereinafter are referred to as EP151, EP151-2, EP151-49, EP151-51 and EP151-52 and the methods for preparing same were as follows:

a. CMC Hydrolysate EP151 was prepared as described in Example 2c(i) hereinabove.

b. CMC Hydrolysate EP151-2

20kg of carboxymethylcellulose (CMC 7LFD-type, a cellulose gum, also designated by the tradename Blanose and available from Hercules Chemical Company, 92507, Rueil-Malmaison Ceder, France, 7LFD designating a low viscosity, food grade sodium carboxymethylcellulose having 7 out of 10 glucose units substituted with carboxymethyl group) was mixed in 250l of water and the pH of the solution was adjusted to 5.8 with 15% phosphoric acid and the temperature raised to 40°C. 0.177l of the above-described *Trichoderma* enzyme preparation, having a total endo-1, 4 beta-glucanase activity of 1,780,000 nkat, was added to the CMC solution. After one hour another 20kg of CMC was added to the solution. After hydrolysis for 23 hours the enzyme was inactivated by heating (90°C, 15 min.). Finally, the hydrolysis solution was concentrated by spray-drying.

c. <u>CMC Hydrolysate EP151-49</u>

6kg of sodium carboxymethylcellulose (CMC Finnfix 5, available from Metsä-Serla, Chemical Division, SF-44100 Äänekoski, Finland, representing food grade purity and having a degree of substitution between 0.6-0.8) was mixed with 240l of water. The pH of the solution was adjusted between 5.5 and 5.9 with 15% of phosphoric acid and the temperature was maintained at 40°C. 65ml of the above-described <u>Trichoderma</u> enzyme preparation, the endo-ß-1,4-glucanase activity of which totalled 539,000 nkat, was added to the CMC solution. After an hour another 6kg of CMC was added. After hydrolysis for 23 hours, the enzyme was inactivated by heating the solution (90°C, 15 min.). The hydrolysate was then concentrated by spray-drying.

d. <u>CMC Hydrolysate EP151-51</u>

6kg of sodium carboxymethylcellulose (CMC Finnfix 5) was mixed with 240l of water. Temperature and pH were as described with reference to preparation of EP151-49 (40°C, pH 5.5-5.9). 130ml of the <u>Trichoderma</u> enzyme preparation, the endo-ß-1,4-glucanase activity of which totalled 1,079,000, was added to the CMC solution. After two hours another 6kg of CMC was added. After hydrolysis for 47 hours the enzyme was inactivated by heating the solution (90°C, 15 min.). The hydrolysate was then concentrated by evaporating and spray-drying.

e. CMC Hydrolysate EP151-52

This hydrolysate was produced as described with reference to EP151-51, except that 195ml of the enzyme preparation containing an endo-ß-1,4-glucanase activity of 1,618,000 nkat was used, and the hydrolysis time was 24 hours.

Average DP Calculation

The viscosities, the intrinsic viscosities, the viscosity average molecular weights and the average degrees of polymerization of these various hydrolysate products are set forth in the following Table 3. The viscosities were determined using a rotational viscometer (Haake Viscotester VT 500 with sensor system NV, Karlsruhe, Federal Republic of Germany). The intrinsic viscosities were measured according to the conventional method (described in Flory, Principles of Polymer Chemistry, Cornell Univ. Press, VII-4a, Ithaca, NY (1953)) at 25°C by using a calibrated Cannon Fenske capillary viscometer (size 50, Cannon Instrument, State College, PA, USA).

The viscosity average molecular weights of the CMC hydrolysates were calculated using the Mark-Houwink equation:

$$[\eta] = KM_v^a$$

where $[\eta]$ is intrinsic viscosity, M_v is the average molecular weight of the polymer and K and a are hydrodynamic constants characteristic of the particular polymer-solvent system. The values of K and a for CMC, which were used in this study, were: K = 0.043 in 0.2M NaCl and a = 0.76 in 0.2M NaCl as described in Brown and Henley, Studies on Cellulose Derivatives Part IV. The Configuration of the Polyelectrolyte Sodium Chloride Solutions, Macromol. Chem., Vol. 79, pp. 68-88 (1964).

TABLE 3

CMC Hydrolysate	Viscosity (mPas)	Intrinsic Viscosity[2] (ml/g)	Average M_v	Average DP
151	32	31.4	7400	39
151-2	20	22.9	4800	25
151-49	23	18.4	3600	19
151-51	18	14.0	2500	13
151-52	18	14.3	2600	13

1) 20% (w/w) solution, 25°C shear rate = 584 s^{-1}
2) measured in 0.2M NaCl, 25°C

It is noted that a variety of methods for determining average molecular weight exist, and therefore the values of average molecular weights determined, as well as the average DP values calculated from them, depend upon the experimental method and the basis of calculation. For example, the number average molecular weight can be determined by end group analysis, osmotic pressure, vapor pressure lowering, boiling point elevation and freezing point depression. The weight average molecular weight can be determined by light scattering experiment, the viscosity average molecular weight from the size exclusion chromatograph. All these methods can be used for determining the average DP values, although different results will be obtained depending on method and calculation used.

For purposes of the present invention and parent U.S. patent application serial nos. 370,629 and 309,387, the average DP values were calculated from the viscosity average molecular weights, which were determined as described above (using K = 0.043 and a = 0.76 for calculation).

Madeira Cake

Following is a conventional ingredient recipe (representing a total batch weight) and method for making a Madeira cake

having normal levels of sugar, fat and/or carbohydrate:

Ingredients	Weight (g)
High ratio cake flour	200
Sugar - caster (sweetener)	250
High ratio shortening	130
Skimmed milk powder	16
Salt	3
Baking powder (raising agent)	12
Water	180
Egg	176

METHOD (using Hobart Laboratory Mixer)

1. Place water, dry ingredients and fat in the bowl
2. Using beater, mix on speed 1 for 30 secs and scrape down
3. Mix on speed 3 for another 30 secs and scrape down
4. Add egg over 30 secs on speed 1 and scrape down
5. Mix on speed 2 until 0.8 specific gravity is obtained
6. Scale 180g into greased tins and bake at 170°C, middle shelf of domestic fan oven for 30 mins.

Utilizing various aqueous solutions of EP151, EP151-2, EP151-49, EP151-51 and EP151-52 of varying concentrations (and therefore, varying viscosity), 40% of the normal high ratio shortening (or fat) ingredient, i.e. 52g of fat or 5.4% of the total batch weight of the above Madeira cake recipe, was replaced with the following listed solutions in an amount so as to achieve a level of dry EP151, EP151-2, EP151-49, EP151-51 or EP151-52 ingredient (solids) as listed below (expressed as

level of dry ingredient used as a percentage of total batch weight):

CMC Hydrolysate Substitute (% by weight in aqueous solution)	Level of fat substitution (% of fat wt)	Level of fat substitution (% of total batch wt)	Level of dry ingredient used (% of total batch wt)
EP151 (40% solids)	40%	5.4%	2.2%
EP151-2 (47% solids)	40%	5.4%	2.5%
EP151-2 (40% solids)	40%	5.4%	2.2%
EP151-49 (46% solids)	40%	5.4%	2.5%
EP151-49 (40% solids)	40%	5.4%	2.2%
EP151-51 (50% solids)	40%	5.4%	2.7%
EP151-51 (40% solids)	40%	5.4%	2.2%
EP151-51 (50% solids)	40%	5.4%	2.7%
EP151-52 (40% solids)	40%	5.4%	2.2%

All of the Madeira cakes produced according to the above-listed substitutions had acceptable appearances, colors, volumes, textures, structures, odors, flavors and mouthfeels. The water activities of the various cakes differed slightly due to the slightly varying amounts and concentrations of the

solutions substituted. Preparations wherein about 40% to about 75% of the fat ingredient is replaced with a substantially equivalent weight amount of a 40% solution of EP 151-51, should produce relatively acceptable cakes. Thus, it is believed that acceptable cakes may be obtained somewhere at a level of 40% - 75% fat replacement with a degraded cellulose derivative mixture of oligomers (average DP 3-300).

As is known in the art with regard to cake mixtures of the sort similar to the specific Madeira cake formulation set forth above, the amount of the major ingredients comprising more than about 10% of the total batch weight, may be varied by about plus or minus 5%, and the ingredients comprising less than about 10% of the total batch weight might typically be varied by about plus or minus 1%. With regard to cake mixtures generally (i.e. other than Madeira cake), flour, sugar (sweetener), shortening (fat), baking powder, water and egg components are typically common to all.

Butter Icing (Frosting)

Following is a conventional ingredient recipe (representing a total batch weight) and method for making a butter icing having normal levels of fat:

Ingredients	Weight (g)
Butter (unsalted)	179
Icing sugar (sweetener)	225
Water	96

METHOD

1. Soften the butter
2. Add icing sugar and cream together
3. Add water slowly and whisk until light and fluffy.

Again utilizing various solutions of EP151, EP151-2, EP151-49, EP151-51 and EP151-52 of varying concentrations, 33% of the fat (butter) ingredient, i.e. 60g or 11.8% of the total batch weight, was replaced with the following listed solutions wherein the following listed amounts of solid EP151, EP151-2, EP151-49, EP151-51 and EP151-52 were added (expressed as level of dry ingredient used as % of total batch weight):

CMC Hydrolysate Substitute (% by weight of aqueous solution	Level of fat substitution (% of fat wt)	Level of fat substitution (% of total batch wt)	Level of dry ingredient used (% of total batch wt)
EP 151 (40% solids)	33%	11.8%	4.7%
EP 151-2 (47% solids)	33%	11.8%	5.5%
EP 151-2 (40% solids)	33%	11.8%	4.7%
EP 151-49 (46% solids)	33%	11.8%	4.7%
EP 151-49 (40% solids)	33%	11.8%	4.7%
EP 151-51 (50% solids)	33%	11.8%	5.9%
EP 151-51 (40% solids)	33%	11.8%	4.7%

EP 151-51 (50% solids)	33%	11.8%	5.9%
EP 151-52 (40% solids)	33%	11.8%	4.7%

All of the butter icings obtained via the above-listed levels of fat replacement were acceptable. Although these icings had slightly higher bulk densities relative to an icing obtained from a conventional recipe, the eating quality was not substantially affected. At 40% fat replacement with EP151-52 a better product was obtained than might be obtained via replacement of the fat with conventional fat sparing agents such as potato maltodextrin. Preparations in which about 30% to about 75% of the fat ingredient of the conventional recipe is substituted with an equivalent weight amount of a 40% solution of EP151-52 should produce relatively acceptable icings. Thus, a butter icing in which about 30% to about 75% of the fat ingredient is replaced with a degraded cellulose derivative oligomeric mixture having an average DP of between about 3 and about 300 produces a low calorie icing of acceptable eating quality. Where greater that about 50% fat replacement is desired, appropriate amounts of a stabilizer and/or an emulsifier should also preferably be included in the recipe.

As is known in the art, the tolerance range for variation of the various components in the typical icing formulation set forth above is plus or minus about 5%.

Mayonnaise

With respect to attempting to obtain a fat substituted low calorie mayonnaise product, the following is an already low calorie (fat reduced) recipe which might be modified by replacing a portion of the water and starch components of the low calorie recipe with an equivalent amount (by weight) of a solution of a degraded cellulose derivative.

Ingredients	Weight (g)
Water	243.0
Vegetable oil	180.00
Instant starch (thickener)	27.0
White vinegar (acidifier)	84.0
Egg Yolk (emulsifier)	48.0
Salt	9.0
Powdered glucose	9.0

METHOD

1. Blend all the dry ingredients and add slowly to the water which is being whipped on a Hobart at medium speed.
2. Heat the solution to 60°C.
3. Cool to 20°C.
4. Add the egg yolk and mix well.
5. Add the chilled oil (10°C) slowly while agitating on the Hobart on medium speed.
6. When most of the oil is added, add vinegar slowly while mixing.

By way of example, one modified reduced calorie recipe of acceptable eating quality was obtained by replacing 54g of the water and 27g of the starch ingredients of the above mayonnaise

recipe with an equivalent amount by weight of a 40% solution of EP151. EP151 may be incorporated into the above reduced calorie recipe up to at least about 15% of the total batch weight. A normal fat mayonnaise recipe typically includes about 2.5 times as much fat (vegetable oil) as the above recipe. Thus, an acceptable low fat mayonnaise can be obtained by replacing from about 25% to about 75% of the fat components with water and an appropriate amount of a degraded cellulose derivative mixture of oligomers having an average DP of between about 3 and about 300.

As is known in the art, mayonnaise formulations generally include at least water, vegetable oil (fat), vinegar (acidifier) and egg yolk (emulsifier); and the major components, water and fat, have a tolerance level of variation of plus or minus about 5%, and the minor components have a tolerance variation level of plus or minus about 1%.

Spreads

With respect to attempting to obtain a fat-reduced spread of better quality, the water component of the following already low fat spread recipe (representing a total batch weight) was modified by substituting a selected amount of a 50% solution of EP151-52 therefor.

Ingredients	Weight (g)
Soft margarine blend (fat)	234.0
Dimodan CP (Emulsifier)	6.0
Water	350.4
Salt	3.6
Sobalg FD120 (Stablilizer)	6.0

METHOD

1. Melt the fat blend and dissolve Dimodan CP into it. Heat to 50°C.
2. Dissolve the salt and Sobalg FD120 into the aqueous phase and heat to 50°C.
3. Place the warm fat phase in a large plastic beaker and insert the large paddle of the motor stirrer.
4. Add the aqueous phase to the fat phase slowly and gradually while stirring at a medium speed. Enough stirring is required to get a good dispersion, but care must be taken to ensure no air is drawn into the mixture.
5. Put the freezing unit of the ice cream maker on for 10 minutes before adding the emulsion.
6. Freeze down for 15 minutes, transfer into plastic tubs and immediately place in a constant temperature 5°C room.

Various levels of EP151-52 solution addition were tested by replacing 12g (2% of total batch weight) 60g (10% of total batch weight), and 120g (20% of total batch weight) of the water component in the above-listed low fat recipe with an equivalent amount by weight of a 50% solution of EP151-52. Up to 20% of total batch weight replacement (i.e. up to 120g) produced a low fat spread of acceptable eating quality. At about 20% total batch weight replacement, the EP151-52 containing low fat spread was better than the recipe above.

Normal fat containing spread typically includes about 79-83% of fat and about 16-20% water (as opposed to the above-listed low fat spread recipe wherein the fat phase is about 25-40% and water is about 58-75% water). Thus an acceptable low fat spread can be obtained by replacing from about 38% to about 75% of the fat components (typically butter and/or vegetable oils) in a normal fat margarine spread with water and an appropriate amount of a degraded cellulose derivative mixture of oligomers having an average DP of between about 3 and about 300. According to the above-described modification and improvement of the already low fat recipe, a normal fat spread recipe can thus suitably be modified by replacing from 38%-75% of the fat component with an equivalent amount by weight of an aqueous solution containing from about 3% to about 70% degraded cellulose derivative, and more preferably, a solution containing from about 30% to about 50% of degraded cellulose derivative material.

As is known in the art, all low fat spread formulations generally include at least fat blend, water, emulsifier and stabilizer ingredients; and, these various major components typically have a tolerance variation level of plus or minus about 1%.

Marzipan

Following is a conventional recipe (representing total

batch weight) and method for making marzipan:

Ingredients	Weight (g)
Icing sugar (carbohydrate)	21.8 g
Caster sugar (carbohydrate)	21.8 g
Ground Almonds	43.7 g
Vanilla Flavoring	0.8 g
Egg	10.9 g
Lemon Juice	0.8 g

The above mixture is formed into a ball, lightly kneaded, rolled out and cut into desired shapes.

Up to about 40% of the icing sugar component may be replaced with an appropriate amount of a degraded cellulose derivative having an average DP of 3-300 and a confection of acceptable eating quality obtained.

Apart from sweet and savoury food products such as cake, icing, cookies, spreads, creams, snack fillings and the like, the degraded cellulose derivatives of the invention should be suitable as high calorie component (fat, carbohydrate) substitutes in relatively high protein containing systems such as meat pate and other meat emulsions, it being recognized that for any given food stuff composition, the particular range of amounts of certain ingredients of the normal high calorie recipe which may be modified to allow a degraded cellulose derivative to be incorporated, is determined to provide an end food product which has an eating quality approaching that of the normal high calorie recipe.

It will now be apparent to those skilled in the art that other embodiments, improvements, details, and uses can be made consistent with the letter and spirit of the foregoing disclosure and within the scope of this patent, which is limited only by the following claims, construed in accordance with the patent law, including the doctrine of equivalents.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A foodstuff composition comprising a mixture of oligomers derived from degradation of a cellulose derivative substituted for at least a portion of a high calorie ingredient originally contained in said foodstuff composition, wherein the mixture of oligomers has an average degree of polymerization in the range of 3 to 300 and the average molecular weight in the range of 500 - 100 000 determined on the basis of intrinsic viscosity.

2. The foodstuff composition of claim 1, wherein the cellulose derivative is selected from the group of carboxymethylcellulose, methylcellulose, methylethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose and mixtures thereof.

3. The foodstuff composition of claim 1, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

4. The foodstuff composition of claim 2, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

5. The foodstuff composition of claim 1, 2, 3 or 4, wherein the high calorie ingredient is selected from the group of fat and carbohydrate.

6. The foodstuff composition of claim 1, wherein less than about 75% of the high calorie ingredient is removed from the food composition.

7. The foodstuff composition of claim 6, wherein at least about 25% of the high calorie ingredient is removed from the food composition.

8. The foodstuff composition of claim 1, wherein the high calorie ingredient is selected from the group of fat and carbohydrate and less than about 75% of the high calorie ingredient is removed from the food composition.

9. The foodstuff composition of claim 8, wherein at least about 25% of the high calorie ingredient is removed from the food composition.

10. A method for reducing the calorie content of a foodstuff composition, comprising substituting a mixture of oligomers derived from degradation of a cellulose derivative for at least a portion of the high calorie ingredient originally contained in the food stuff composition, wherein the mixture of oligomers has an average degree of polymerization in the range of 3 to 300, and the average molecular weight in the range of 500 - 100 000 determined on the basis of intrinsic viscosity.

11. The method of claim 10, wherein the cellulose derivative is selected from the group of carboxymethylcellulose, methylcellulose, methylethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose and mixtures thereof.

12. The method of claim 10, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

13. The method of claim 13, wherein the mixture

of oligomers has an average degree of polymerization in the range of 5 to 100.

14. The method of claim 10, 11, 12 or 13, wherein the high calorie ingredient is selected from the group of fat and carbohydrate.

15. The method of claim 10, wherein less than about 75% of the high calorie ingredient is removed from the food composition.

16. The method of claim 15, wherein at least about 25% of the high calorie ingredient is removed from the food composition.

17. The method of claim 10, wherein the high calorie ingredient is selected from the group of fat and carbohydrate, and wherein less than about 75% of the high calorie ingredient is removed from the food composition.

18. The method of claim 17, wherein at least about 25% of the high calorie ingredient is removed from the food composition.

19. A foodstuff composition comprising a fat ingredient, water and one or more additional ingredients selected from the group of sweeteners, flours, emulsifiers, raising agents, thickeners, acidifiers and stabilizers, wherein at least a portion of the fat ingredient is substituted by a mixture of oligomers derived from a degraded cellulose derivative, the oligomeric mixture having an average degree of polymerization in the range of 3 to 300 and an average molecular weight in the range of 500-100,000 determined on the basis of intrinsic vicosity.

20. The composition of claim 19, wherein the cellulose derivative is selected from the group of carboxymethylcellulose, methylcellulose, methylethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose and mixtures thereof.

21. The composition of claim 19, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

22. The composition of claim 20, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

23. The composition of claim 19, 20, 21 or 22, wherein less than about 75% of the fat ingredient is removed from the composition.

24. The composition of claim 19, 20, 21 or 22, wherein less than about 75% of the fat ingredient is removed from the composition and wherein at least about 25% of the fat ingredient is removed from the composition.

25. A cake composition comprising:

(a) a fat ingredient;
(b) a sweetener;
(c) a flour;
(d) a raising agent;
(e) egg ingredient; and
(f) water

wherein at least a portion of the fat ingredient is substituted by a mixture of oligomers derived from a degraded cellulose derivative, the oligomeric mixture having an average degree of polymerization in the range of 3 to 300

and an average molecular weight in the range of 500 - 100,000 determined on the basis of intrinsic viscosity.

26. The cake composition of claim 25, wherein the cellulose derivative is selected from the group of carboxymethylcellulose, methylcellulose, methylethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose and mixtures thereof.

27. The cake composition of claim 25, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

28. The cake composition of claim 26, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

29. The cake composition of claim 25, 26, 27 or 28, wherein less than about 75% of the fat ingredient is removed from the composition.

30. The cake composition of claim 25, 26, 27 or 28, wherein less than about 75% of the fat ingredient is removed from the composition and wherein at least about 25% of the fat ingredient is removed from the composition.

31. An icing composition comprising:

(a) a fat ingredient;

(b) a sweetener; and

(c) water

wherein at least a portion of the fat ingredient is substituted by a mixture of oligomers derived from a degraded cellulose derivative, the oligomeric mixture having

an average degree of polymerization in the range of 3 to 300 and an average molecular weight in the range of 500 - 100,000 determined on the basis of intrinsic viscosity.

32. The composition of claim 31, wherein the cellulose derivative is selected from the group of carboxymethylcellulose, methylcellulose, methylethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose and mixtures thereof.

33. The composition of claim 31, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

34. The composition of claim 32, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

35. The composition of claim 31, 32, 33 or 34, wherein less than about 75% of the fat ingredient is removed from the composition.

36. The composition of claim 31, 32, 33 or 34, wherein less than about 75% of the fat ingredient is removed from the composition at least about 25% of the fat ingredient is removed from the composition.

37. A mayonnaise composition comprising:

(a) a fat ingredient;

(b) a thickener;

(c) an acidifier;

(d) an emulsifier; and

(e) water

wherein at least a portion of the fat ingredient is substituted by a mixture of oligomers derived from a degraded cellulose derivative, the oligomeric mixture having an average degree of polymerization in the range of 3 to 300 and an average molecular weight in the range of 500 - 100,000 determined on the basis of intrinsic viscosity.

38. The composition of claim 37, wherein the cellulose derivative is selected from the group of carboxymethylcellulose, methylcellulose, methylethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose and mixtures thereof.

39. The composition of claim 37, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

40. The composition of claim 38, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

41. The composition of claim 37, 38, 39, 40, wherein less than about 75% of the fat ingredient is removed from the composition.

42. The composition of claim 37, 38, 39 or 40, wherein less than about 75% of the fat ingredient is removed from the composition, and wherein at least about 25% of the fat ingredient is removed from the composition.

43. A spread composition comprising:

(a) a fat ingredient;

(b) water

wherein at least a portion of the fat ingredient is substituted by a mixture of oligomers derived from a degraded cellulose derivative, the oligomeric mixture having an average degree of polymerization in the range of 3 to 300 and an average molecular weight in the range of 500 - 100,000 determined on the basis of intrinsic viscosity.

44. The composition of claim 43, wherein the cellulose derivative is selected from the group of carboxymethylcellulose, methylcellulose, methylethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose and mixtures thereof.

45. The composition of claim 43, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

46. The composition of claim 44, wherein the mixture of oligomers has an average degree of polymerization in the range of 5 to 100.

47. The composition of claim 43, 44, 45 or 46 further comprising:
(c) an emulsifier.

48. The composition of claim 43, 44, 45 or 46 further comprising:
(d) a stabilizer.

49. The composition of claim 43, 44, 45 or 46 further comprising:
(c) an emulsifier, and
(d) a stabilizer.

50. The composition of claim 43, 44, 45 or 46, wherein less than about 50% of the fat ingredient is removed from the composition.

51. The composition of claim 50, wherein less than about 50% of the fat ingredient is removed from the composition and wherein at least about 25% of the fat ingredient is removed from the composition.

52. The composition of any of claim 1 to 4 and 6 to 9, wherein the oligomeric mixture is produced by hydrolyzing the cellulose derivative with an enzymatic cellulase preparation.

53. The method of any of claim 10 to 13 and 15 to 18, wherein the oligomeric mixture is produced by hydrolyzing the cellulose derivative with an enzymatic cellulase preparation.

54. The composition of any of claim 19 to 22, 25 to 28, 31 to 34, 37 to 40 and 43 to 46, wherein the oligomeric mixture is produced by hydrolyzing the cellulose derivative with an enzymatic cellulase preparation.

55. The composition of any of claim 1 to 4 and 6 to 9, wherein the oligomeric mixture is produced by chemical hydrolysis or physical degradation of the cellulose derivative.

56. The method of any of claim 1 to 13 and 15 to 18, wherein the oligomeric mixture is produced by chemical hydrolysis or physical degradation of the cellulose derivative.

57. The composition of any of claim 19 to 22, 25 to 28, 31 to 34, 37 to 40 and 43 to 46, wherein the oligomeric mixture is produced by chemical hydrolysis or physical degradation of the cellulose derivative.

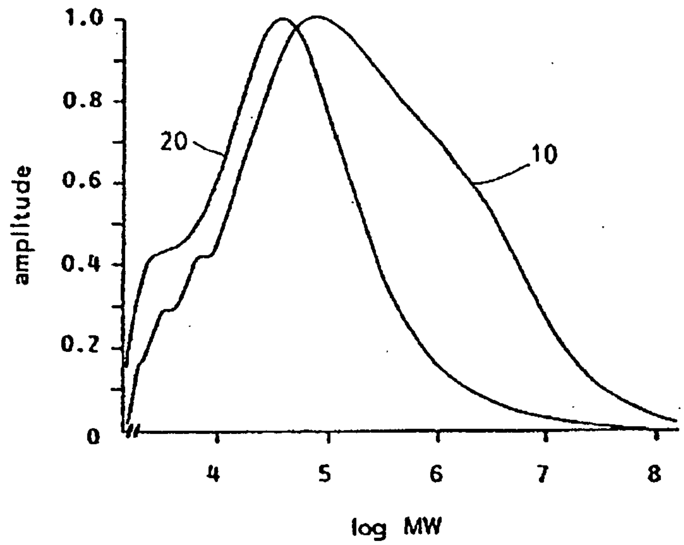
58. A method for preparing a low calorie food product comprising replacing at least a portion of a high calorie ingredient of a high calorie foodstuff composition with a mixture of oligomers derived from degradation of a cellulose derivative, the mixture of oligomers having an average degree of polymerization in the range of 3 to 300 and the average molecular weight in the range of 500 - 100 000 determined on the basis of intrinsic viscosity.

59. The method of claim 58, wherein the high calorie ingredient is selected from the group of fat and carbohydrate.

60. The method of claim 58 or 59, wherein the cellulose derivative is selected from the group of carboxymethylcellulose, methylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose and mixtures thereof.

61. The method of claim 58 or 59, wherein between about 25% and about 75% of the high calorie ingredient is replaced.

62. The method of claim 58 or 59, wherein the cellulose derivative is selected from the group of carboxymethylcellulose, methylcellulose, methylethylcellulose hydroxypropylcellulose, hydroxypropylmethylcellulose and mixtures thereof and wherein between about 25% and about 75% of the high calorie ingredient is replaced.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log MW

FIG. 1

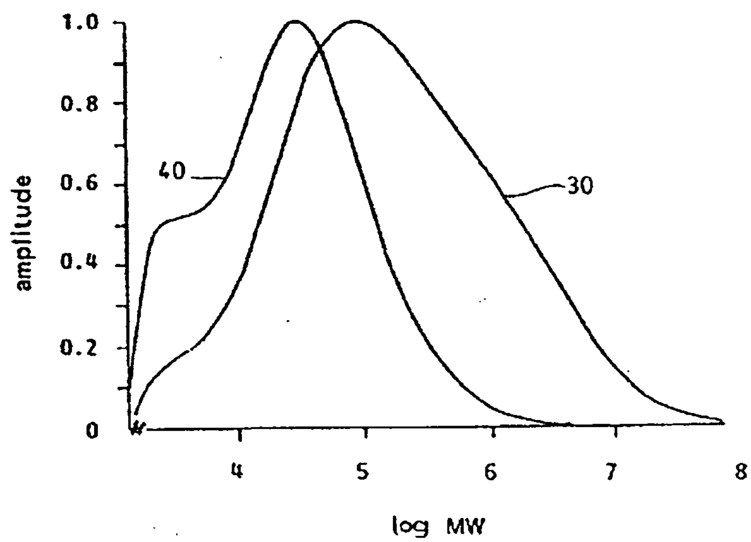
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FIG. 2

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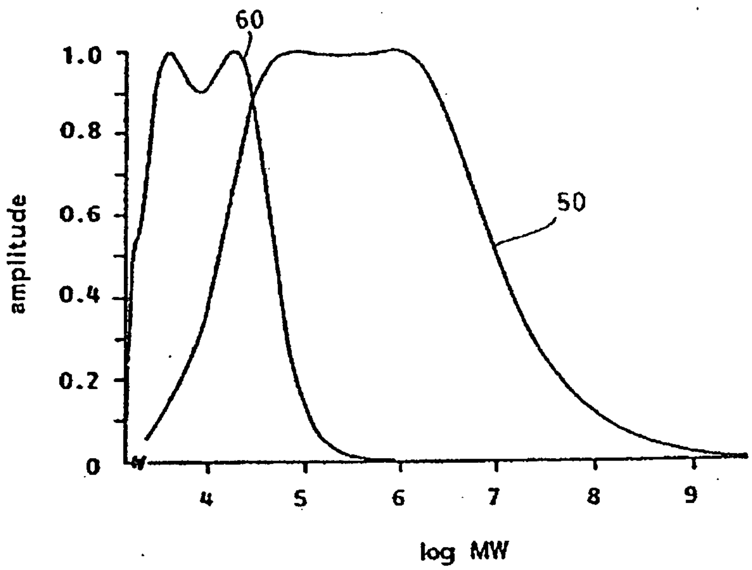

FIG. 3

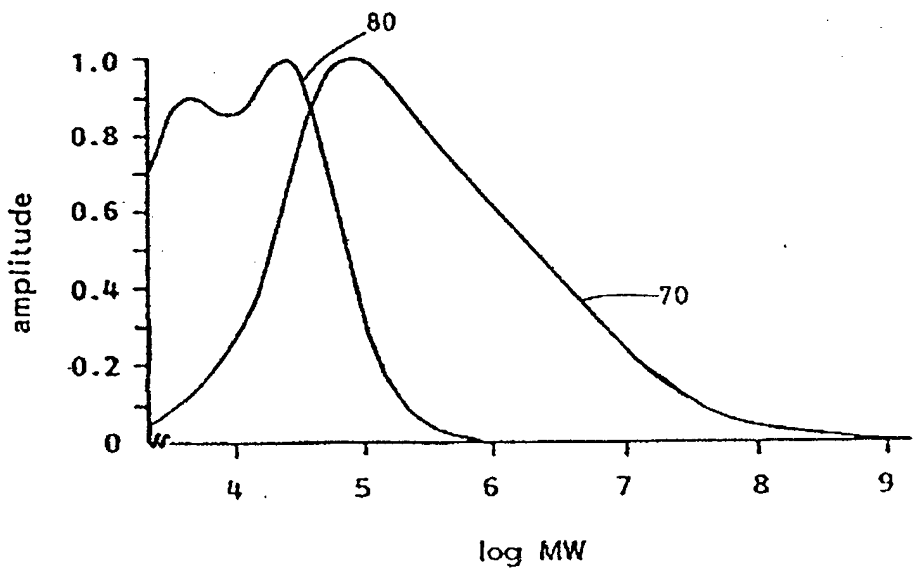

FIG. 4

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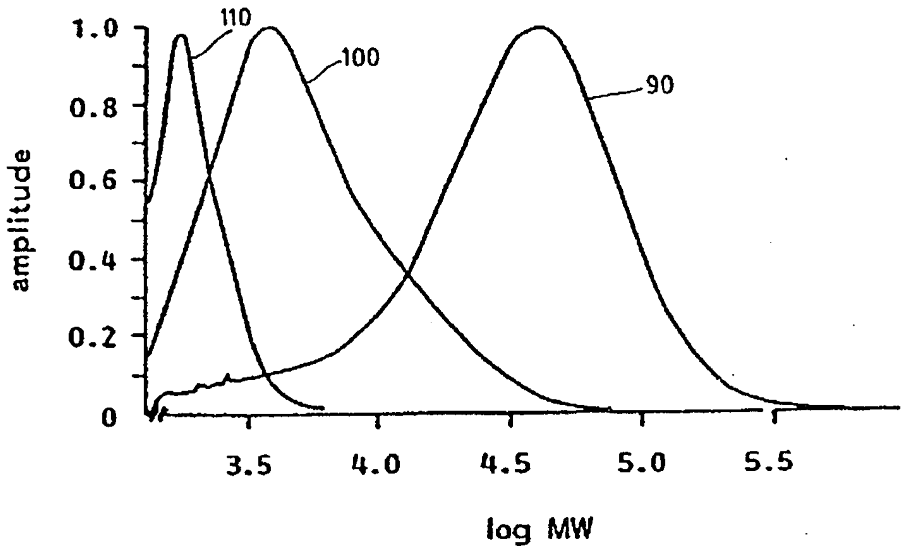

FIG. 5